(12) EUROPEAN PATENT APPLICATION

(71) Applicant: MOBIL OIL CORPORATION
3225 Gallows Road
Fairfax Virginia 22037(US)

(72) Inventor: Calabro, David Charles
4 Tunnell Road
Somerset, New Jersey 08873(US)
Inventor: Cook, Pamela Jean
20 Quail Run
Jamesburg, New Jersey 08831(US)
Inventor: Kral, Bohumil Vaclav
631 Smith Street, P.O. Box 55
Sour Lake, Texas 77659(US)

(74) Representative: Colmer, Stephen Gary et al
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(54) **Broad distribution, high molecular weight low density polyethylene and method of making thereof.**

(57) There is disclosed a low density polymer having a broad molecular weight distribution, such that its melt flow ratio (MFR) is about 50 to about 250, and a substantially constant melt index-corrected density. The polymer, produced e.g., by blending a first polymer component of high molecular weight with a second polymer component of low molecular weight, with both polymer components having substantially the same melt index-corrected density, produces films having improved strength properties and low hexane extractables, as compared to films made from comparable individual polymer components. There is also disclosed a low density polymer, also having MFR of about 50 to about 250, having substantially no polymer chains having low molecular weight and short chain branches, which is prepared by blending a first polymer component of low density and high molecular weight with a second polymer component of relatively high density and relatively low molecular weight. The melt index-corrected densities of these two polymer components are dissimilar.

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BROAD DISTRIBUTION, HIGH MOLECULAR WEIGHT LOW DENSITY POLYETHYLENE AND METHOD OF MAKING THEREOF

This invention relates to low density polymers having broad molecular weight distributions and substantially uniform branching frequencies, and to a method of preparation thereof. More particularly, the invention relates to low density polyethylenes having a broad molecular weight distribution and excellent strength properties, but relatively low level of hexane extractables.

High density polyethylene (HDPE) polymers having broad molecular weight distribution and high molecular weight have been proposed in the past. Such polymers are usually made by blending a high molecular weight, high density component with a low molecular weight, high density component. These blends have good physical properties, derived from the high molecular weight component, and good processability, provided by the low molecular weight component. However, such a method of producing the broad molecular weight distribution products is restricted to high density polymers because is is believed in the art that if low density, broad molecular weight distribution polymers were made by blending a high molecular weight, low density component with a low molecular weight, low density component, the resulting blend would produce end use products, such as films, having high hexane extractables. High hexane extractables are undesirable because films and other articles made from such polymers may not meet strict Food and Drug Administration (FDA) requirements which limit the amount of hexane extractables. Additionally, high levels of hexane extractables may cause operational difficulties, for example, in extruders the extractable material tends to separate out in the die and drip therefrom.

It is also known that low density and medium density copolymers of ethylene with minor amounts of higher alpha-olefins, such as C_3 to C_{10} alpha-olefin; for example, 1-hexene or 1-octene, have good strength properties, for example, good tear strength resistance. However, such polymers have relatively narrow molecular weight distribution which is undesirable in some applications, for example, wherein broad molecular weight distribution is needed to exploit the benefits of the high molecular weight fraction, such as increased film strength.

This invention seeks to provide a low density polymer, particularly linear low density polyethylene (LLDPE), having relatively broad molecular weight distribution, and therefore good processibility at high molecular weights. This combination of low density and broad molecular weight distribution provides exceptional impact strength, tear resistance, and relatively low levels of hexane extractables.

In accordance with one aspect of this invention, there is provided a low density polymer, particularly a linear low density polymer (LLDPE), which has a broad molecular weight distribution, such that its melt flow ratio (MFR) is from 50 to 250, and a substantially constant melt index-corrected density of substantially all of its components throughout the molecular weight distribution of the polymer. Films manufactured from the polymer have excellent strength properties and relatively low hexane extractables.

In accordance with a further aspect of this invention, there is provided, as a first process embodiment, a process for producing the aforementioned polymer which process comprises blending a first polymer component of high molecular weight with a second polymer component of low molecular weight, the first and the second polymer components having substantially the same melt index-corrected density. Since both the first and the second polymer components have substantially the same melt index-corrected density, the branching frequency of both polymers is believed to be substantially constant.

An alternative process in accordance with this embodiment comprises polymerizing an olefin or a mixture of olefins in the presence of a first, suitably a Ziegler-Natta, catalyst composition to a second polymer component having low molecular weight, and subsequently polymerizing an olefin or a mixture of olefins in the presence of the same or different catalyst composition to a first polymer component having high molecular weight, the first and the second polymer components having substantially the same melt index-corrected density, to obtain the low density polymer of this invention. The product has a substantially constant branching frequency throughout the molecular weight distribution of the polymer.

In accordance with a still further aspect of this invention, there is provided, as a second process embodiment, a process for producing the aforementioned polymer which process comprises blending a first polymer component of high molecular weight, which is preferably LLDPE having a density from 0.880 to 0.930 g/cc and a high load melt index of 0.1 to 3.0 g/min. with a second polymer component of low molecular weight having a density from 0.940 to 0.970 g/cc, and a melt index from 100 to 1000 g/10 min. This alternative polymer also produces films having excellent strength properties and relatively low hexane extractables.

The polymers of all embodiments of this invention have broad molecular weight distribution, as demonstrated by the melt flow ratio thereof being from 50 to 250, preferably 70 to 200 and most preferably

from 80 to 160.

First Embodiment (Polymer Made From Two Components of Substantially The Same Melt Index-Corrected Density)

The polymer of the first embodiment of the invention has a substantially constant melt index-corrected density throughout the molecular weight distribution of the polymer. The term "substantially constant melt index-corrected density throughout the molecular weight distribution of the polymer" means that the number of short chain branches is substantially constant throughout the polymer. The high molecular weight component and the low molecular weight component have substantially the same frequency of branches, i.e., the number of branches per 1000 carbon atoms of the backbone chains of both components is substantially the same. Measured density is dependent on molecular weight, so by "correcting" the density, of both components to melt index (I_2) = 1.0, the molecular-weight dependence is eliminated and the corrected density is only a function of branch content. Generally, the melt index-corrected density is the density that would be obtained if the melt index (I_2) of both components was 1.0.

Substantially constant melt index-corrected density is obtained by choosing components that have the desired melt index and measured densities that will result in a constant melt index-corrected density. The constant melt index-corrected density, i.e., the density normalized to melt index (I_2) = 1.0, is calculated from the following equation:

$$d_c = d - 0.0105 \, [1-(I_2)^{-0.28}]$$

where d_c is melt index - corrected density;

d is measured density;

I_2 is melt index.

For example, if the first polymer component has a high load melt index (I_{21}) of 0.4, and the second polymer component has a melt index (I_2) of about 100, to obtain a polymer product having melt index-corrected density of 0.932 g/cc, the measured densities of the first and second polymer components would have to be 0.904 and 0.937 g/cc, respectively. The melt index-corrected density of the first and second polymer components would be 0.932 g/cc. If the proportions of the first polymer component and the second component were such that the final blend high load melt index (I_{21}) was 7.0, then the measured density of the final polymer product would be 0.918 g/cc. Thus, the polymer of this embodiment has measured density 0.900 to 0.940, preferably from 0.915 to 0.930, and most preferably from 0.918 to 0.925 g/cc, and high load melt index (I_{21}) from 3.0 to 25.0, preferably from 5.0 to 15.0 and most preferably from 6.0 to 10.0 g/10 min. It is believed that the constant branching frequency imparts outstanding strength characteristics to the polymer of this embodiment of the invention.

The polymer of this embodiment can be produced by any suitable means, for example, by blending together two separate polymer components, the first polymer component having a high molecular weight and the second polymer component having a low molecular weight, providing that both, the first and the second polymer components have substantially the same melt index-corrected density. The molecular weight of the first polymer component is relatively high, as indicated by the high load melt index (I_{21}) thereof from 0.1 to 3.0, preferably 0.1 to 1.0, most preferably from 0.2 to 1.0 g/cc. The measured density of the first polymer component is from 0.880 to 0.930, preferably from 0.890 to 0.920, and most preferably from 0.900 to 0.915 g/cc. The molecular weight of the second polymer component is relatively low, as indicated by the melt index (I_2) thereof from 100 to 1,000, preferably from 100 to 700 and most preferably from 200 to 500 g/10 min. The measured density of the second polymer component is from 0.900 to 0.950, preferably from 0.920 to 0.945, and most preferably from 0.920 to 0.935 g/cc. Since the final polymer product of this embodiment has measured density from 0.900 to 0.940, preferably from 0.915 to 0.930, and most preferably from 0.918 to 0.925 g/cc, the melt index-corrected density of the first polymer component and the second polymer component and, therefore, the polymer product of this embodiment is from 0.890 to 0.940, preferably from 0.910 to 0.940 and most preferably from 0.915 to 0.930 g/cc. The blending is carried out in a conventional manner, for example, by initially dry blending the resin in a mixer with suitable additives, and then melt blending it in an extruder. The relative proportions of the first and second polymer components are such that the blending produces the polymer product having the aforementioned properties.

Alternatively, the polymer of this embodiment can also be produced by sequentially polymerizing the two polymer components in the presence of the same or different olefin polymerization catalyst, such as any Ziegler-Natta catalyst which produces polymers of narrow molecular weight distribution. For example,

initially the second polymer component, defined above, of low molecular weight is produced in the presence of an olefin polymerization catalyst and with a substantial amount of added hydrogen in the polymerization reactor. Subsequently, the first polymer component, also defined above, having high molecular weight is polymerized in the same reactor as the second polymer component or in a separate reactor in the presence of a catalyst and reactor conditions (such as the amount of hydrogen) which are the same as or different than the catalyst and the reactor conditions used to polymerize the second polymer component. The relative amounts of the first and second polymer components produced in this alternative method are such that the polymer product has the aforementioned properties. Films made from the polymer of this embodiment exhibit synergistically better strength properties, such as tear resistance properties, than films made from single-component resins of somewhat higher density and similar or substantially higher flow index (I_{21}).

Second Embodiment (Polymer Made From Two Components of Dissimilar Melt-Index Corrected Density)

The relatively broad molecular weight distribution polymer of this embodiment, having the same melt flow ratio as the polymer of the first embodiment, has a measured density from 0.910 to 0.940, preferably from 0.915 to 0.940, and most preferably from 0.920 to 0.940 g/cc, and high load melt index (I_{21}) from 3.0 to 25.0, preferably from 5.0 to 15, and most preferably from 6.0 to 10.0 g/10 min. This polymer is made by blending a first polymer component having relatively high molecular weight and relatively low density with a second polymer component having relatively low molecular weight and relatively high density. The first polymer component has high load melt index (I_{21}) from 0.1 to 3.0, preferably from 0.1 to 1.0, and most preferably from 0.2 to 1.0 g/10 min, and density from 0.880 to 0.930, preferably from 0.890 to 0.920, and most preferably from 0.900 to 0.915 g/cc. The melt index-corrected density of the first polymer component is about 0.890 to about 0.940, preferably from 0.910 to 0.940, and most preferably from 0.915 to 0.930 g/cc. The second polymer component has melt index (I_2) from 100 to 1,000, preferably from 100 to 700, and most preferably from 200 to 500 g/10 min, and a density from, 0.940 to 0.970, preferably from 0.950 to 0.970, and most preferably from 0.960 to 0.970 g/cc. The melt index-corrected density of the second polymer component is from 0.930 to 0.970, preferably from 0.940 to 0.970, and most preferably from 0.950 to 0.970 g/cc. The relative proportions of the first and second polymer components are such as to produce the final polymer product having the aforementioned properties. The polymer product of this embodiment also produces films having excellent strength properties, as compared to the films made from single component resins of similar density and melt index.

Additionally, the polymer product of this embodiment has relatively low levels of extractables. The chemical nature of the extractables is also changed; in particular, the extractable material of this polymer product has weight average molecular weight about an order of magnitude higher than the polymer of the single component resin, and it contains substantially no polymer chains having both low molecular weight (1,000 to 10,000) and a significant number of short chain branches; that is chain branches of either 2 or 4 carbons in length, usually introduced into the polymer by a copolymer, e.g., 1-butene or 1-hexene.

Conventional additives, such as antioxidants, can be used in the preparation of the polymers of all embodiments of this invention.

The following Examples illustrate the invention:

The properties of the polymers produced in the Examples and any calculated process parameters were determined by the following test methods:

Density: ASTM D 1505--A plaque is made and conditioned for one hour at 100 °C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as g/cc.

Melt Index (MI), I_2: ASTM D-1238--Condition E--Measured at 190 °C--reported as/10 min.

High Load Melt Index (HLMI), I_{21}: ASTM D-1238--Condition F--Measured at 10.5 times the weight used in the melt index test above.

Melt Flow Ratio (MFR) = I_{21}/I_2.

N-hexane extractables (FDA test used for polyethylene film intended for food contact applications): A 200 square inch sample of 1.5 mil gauge film is cut into strips measuring 1" x 6" and weighed to the nearest 0.1mg. The strips are placed in a vessel and extracted with 300 ml of n-hexane at 50 ° ± 1 °C for 2 hours. The extract is then decanted into tared culture dishes. After drying the extract in a vacuum desiccator, the culture dish is weighed to the nearest 0.1 mg. The extractables, normalized with respect to the original sample weight, is then reported as the weight fraction of n-hexane extractables.

Machine Direction Tear, MD_{tear}(gm/mil): ASTM D-1922.

EXAMPLES 1 TO 5 AND 6 (COMPARATIVE)

In Examples 1 to 5 two polymer components, component 1 and component 2, were dry blended together with antioxidants to inhibit degradation, then passed through a 3/4" twin screw Brabender extruder. The extrudate was extruded a second time to ensure intimate mixing and to produce a final polymer in the proportions designated in Table 1. All of the polymers in these Examples were copolymers of ethylene and the comonomer indicated in Table 1. The strength properties, such as MD tear and impact tear resistance, and percent extractables of the resulting blended polymers were then compared to the commercial ethylene/1-hexene copolymer (Exxon 44.87, which is a commercial medium density high molecular weight film resin; "EXXON" is a registered trade mark), and the results summarized in Table 1 below.

TABLE 1

PROPERTIES OF LOW DENSITY, BROAD MW DISTRIBUTION POLYETHYLENES
BLENDED SAMPLES VERSUS COMMERCIAL, SINGLE COMPONENT RESIN

Example	1	2	3	4	5	6 (Comparative)
Blend of Components	A&b	A&c	B&a	B&b	B&c	Exxon 44.87
Component 1	A	A	B	B	B	----
Comonomer	Butene	Butene	Hexene	Hexene	Hexene	Hexene
Density (g/cc)	0.912	0.912	0.904	0.904	0.904	----
Melt Index (I_{21} g/10 min)	0.39	0.39	0.38	0.38	0.38	----
*Corr. Density (g/cc)	0.937	0.937	0.929	0.929	0.929	
Fraction of Comp. I	0.65	0.66	0.63	0.64	0.66	----
Component 2	b	c	a	b	c	----
Comonomer	Butene	Homopmr	Hexene	Butene	Homopmr	----
Density (g/cc)	0.933	0.97	0.937	0.933	0.97	----
Melt Index (I_2; g/10 min)	90	105	76	90	105	----
*Corr. Density (g/cc)	0.925	0.962	0.930	0.925	0.962	
Fraction of Comp. 2	0.35	0.34	0.37	0.36	0.34	----
Final Blend						
Density (g/cc)	0	0.934	0.918	0.916	0.924	0.937
I_{21} (g/10 min)	4.14	7.01	7.18	5.37	4.02	7.1
MFR	122	125	163	158	139	92
MD Tear (gms)	111	64	108	109	90	38
Impact (gms)	1390	1280	**	**	1480	260
% Extractables						
Hexane (%)	2.63	1.03	4.77	4.52	2.77	0.62

*Designates melt index-corrected density.
**None of the samples ruptured upon impact, value >1400.

The data of Table 1 indicates that the blends of the two components produce polymers which, when manufactured into films, have tear and impact properties better than the single-component Exxon resin of similar density and melt index, e.g., compare the blend of Example 2 to the Comparative Example 6 and the Example 5 blend to the Comparative Example 6.

Examples 2 and 5 represent an illustration of the second embodiment of this invention in which the branches were concentrated on the high molecular weight end. Examples 1, 3 and 4 are representative of blends with substantially constant melt index-corrected density throughout the molecular weight distribution

of the polymer. These examples indicate that the polymers have exceptional strength properties. No known commercial resins having low density and broad molecular weight distribution exist.

Claims

1. A low density polymer having a broad molecular weight distribution, such that its melt flow ratio is from 50 to 250, and a substantially constant melt index-corrected density throughout the molecular weight distribution of the polymer.

2. A polymer according to claim 1 which has a melt flow ratio from 70 to 200.

3. A polymer according to claim 1 or 2 which has a measured density from 0.900 to 0.940 g/cc.

4. A polymer according to any preceding claim which comprises an olefin polymer.

5. A polymer according to claim 4 which comprises an ethylene polymer.

6. A polymer according to claim 5 which comprises a polymer of ethylene with a minor amount of a C_3 to C_{10} olefin.

7. A process for producing a polymer having a broad molecular weight distribution, such that its melt flow ratio is from 50 to 250, and a substantially constant melt index-corrected density throughout the molecular weight distribution of the polymer, which process comprises blending a first polymer component of high molecular weight with a second polymer component of low molecular weight, the first and the second polymer components having substantially the same melt index-corrected density.

8. A process for producing a polymer having a broad molecular weight distribution, such that its melt flow ratio is from 50 to 250, and a substantially constant melt index-corrected density throughout the molecular weight distribution of the polymer, which process comprises polymerizing an olefin or a mixture of olefins in the presence of a first catalyst composition to a second polymer component having a low molecular weight, and subsequently polymerizing an olefin or a mixture of olefins in the presence of the same or a different catalyst composition to a first polymer component having high molecular weight, the first and the second polymer components having substantially the same melt index-corrected density.

9. A process according to claim 7 or 8 wherein the polymer has substantially the same melt index-corrected density as the first and the second polymer components.

10. A process according to claim 7, or 8 or 9 wherein the first polymer component has a high load index from 0.1 to 3.0 g/10 min.

11. A process according to any of claims 7 to 10 wherein the second polymer component has a melt index from 100 to 1,000 g/10 min.

12. A process according to any of claims 7 to 11 wherein the melt index-corrected density of the first and the second polymer components is from 0.890 to 0.940 g/cc.

13. A low density polymer having a broad molecular weight distribution, such that its melt flow ratio is from 50 to 250 and its density is from 0.910 to 0.940 g/cc.

14. A process for producing a polymer having a broad molecular weight distribution and a melt flow ratio from 50 to 250 which process comprises blending a first polymer component of high molecular weight having a density of 0.880 to 0.930 g/cc and a high load of melt index 0.1 to 3.0 g/10 min. with a second polymer component of low molecular weight having a density of from 0.940 to 0.970 g/cc and a melt index of 100 to 1,000 g/10 min.

15. A film prepared from the polymer of any of claims 1 to 6 or 13.

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Application Number

**EUROPEAN SEARCH
REPORT**

EP 90 31 4179

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with Indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 057 891 (SUMITOMO CHEMICAL COMPANY LIMITED) * page 12, line 25 - page 13, line 12 * * page 15, lines 7 - 9 @ page 30, line 23 - page 31, line 23; claims *	1-15	C 08 L 23/04 C 08 F 297/08
X	GB-A-2 056 996 (ASAHI KASEI KOGYO) * page 1, lines 3 - 11 * * page 2, lines 21 - 46; claims *	1-15	
X	EP-A-0 134 427 (IDEMITSU PETROCHEMICAL COMPANY LIMITED) * page 1, lines 11 - 19 * * page 5, paragraph 4 - page 6, paragraph 1; claims *	1-14	
X	EP-A-0 057 420 (SUMITOMO CHEMICAL INDUSTRIES LTD.) * page 13, lines 19 - 23 * * page 15, line 22 - page 16, line 5; claim 1 * *abstract *	8	

	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
	C 08 L C 08 J C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	21 March 91	CLEMENTE GARCIA R.